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Selective Adsorption of Precious Metals on Sulfur-Containing Chitosan Derivatives

Yoshinari BABA,* Hiroyuki HIRAKAWA,† and Yoshinobu KAWANO
Department of Material Engineering, Faculty of Engineering,
Miyazaki University, Gaguen Kibanadai Nishi 1-1, Miyazaki 889-21
†Department of Applied Chemistry, Faculty of Science & Engineering,
Saga University, Honjo-machi, Saga 840

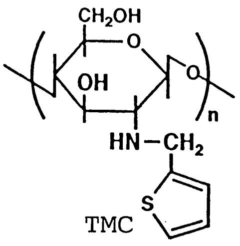
2-Thienylchitosan and 3-(methylthio)propylchitosan were newly synthesized by crosslinking the corresponding Schiff base derivative before reducing it so that the adsorptive activity was not lowered by the crosslinking. These chitosan derivatives selectively adsorbed gold(III), palladium(II) and platinum(IV) over base metals from hydrochloric acid.

The precious metals, especially, gold(III), palladium(II), platinum(IV) are very important metals in industry.1) These metals occur in the nature associated with the major base metals such as copper, nickel, and cobalt, therefore, it is important from both technical and commercial considerations that the individual precious metals are separated not only from the base metals but also from each other to a high purity and with a high percentage of recovery. From such point of view, it is desired to develop new collectors with high selectivity for these metals.

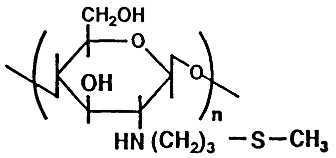
In recent years, since chitosan, a natural chelating polymer, has been employed as an adsorbent for the recovery and purification of metal ions by Muzzarelli et al.,2,3) this polymer has received much attention with respect to use for the removal of harmful heavy metals or radionuclides as well as the recovery of useful metals from industrial waste water. In an earlier paper,4) authors have found that N-(2-pyridylmethyl)chitosan(PMC), which was crosslinked by protecting amino group of chitosan through the Schiff base formation, can effectively adsorb precious metals such as palladium(II) and platinum(IV), and harmful mercury(II). However, the selectivity for these metals in the region of high concentration of hydrochloric acid is very low, PMC can not be available for the separation and purification of precious metals as a high selective adsorbent. Therefore, it is necessary that a better adsorbent with a higher selectivity for precious metals is developed for recovery and purification of ones. Furthermore, thus far a number of chitosan derivatives for metals have been developed,[5] however, few studies on the chitosan derivatives which contain a planar sulfur atom or sulfur atom of a ether type as ligating one have been reported on the adsorption of precious metals.

In the present paper, we newly synthesized the sulfur-containing chitosan derivatives as expected to have a high selectivity for precious metals from the concept of HSAB,[6] and examined their adsorption characteristics for various metals.

2-Thiophenecarboxaldehyde and 3-(methylthio)propionaldehde were supplied from Tokyo Kasei Ltd. Co., and used without further purification. The metal solutions were prepared by dissolving reagent grade of each corresponding metal chloride into hydrochloric acid. Samples of chitosan powder from shells of prawns were kindly donated from Katokichi Co., Ltd., Kan-onji, Japan. The degree of deacetylation of the sample was greater than 95% and it was used as delivered without further purification. Other reagents of reagent grade were used without further purification. All aqueous solutions were prepared with distilled and deionized water. In a similar manner as the earlier paper,[4] N-(2-thienylmethyl)chitosan(TMC) and N-(3-methylthio)propylchitosan(MTPC) were prepared by way of their intermediates which were obtained through the formation reaction of Schiff base between the amino groups of chitosan and the corresponding aldehyde derivatives. The final products, TMC and MTPC, were washed with ethanol and then with deionized water to neutrality. After drying them in vacuo, they were ground and sieved to smaller than 100 mesh size. The intermediates and the final products were identified by IR spectra. In the IR spectra of TMC, the characteristic peaks appeared at around 1634 cm^{-1} and 765 cm^{-1} due to the resulting C=N linkage and substituted thienyl group, respectively. In the IR spectra of MTPC, a characteristic peak appeared at around 1652 cm^{-1} due to the resulting C=N linkage. The reduction of each Schiff base was confirmed by the disappearance of each peak of C=N linkage. The degree of substitution for these chitosan derivatives was determined to be more than 0.90 by elemental analysis of the corresponding Schiff base intermediates.



TMC



MTPC

About 0.1 g of chitosan derivatives sieved and 20 ml of aqueous solution containing metal ion were shaken in a stoppered glass flask of 50 ml immersed in a thermostated water bath maintained at 30 °C overnight to achieve equilibration. From the preliminary experiments, equilibrium was confirmed to have been attained within the period of shaking for all cases. The initial metal concentration was adjusted to 1 mmol dm^{-3} by dissolving metal chloride in 0.01-6 mol dm^{-3} of hydrochloric acid. The initial and equilibrium metal concentrations in the aqueous solutions were determined by titration with EDTA or by using a Seiko(Hamamatsu, Japan) model SPS-7500 atomic absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the concentration change in the aqueous solution before and after the adsorption, volume of the aqueous solutions(20 ml) and the weight of the dry chitosan derivative. The hydrochloric acid concentration was measured by neutralization titration.

Figures 1 and 2 show the relation between the equilibrium concentration of hydrochloric acid and the amount of adsorbed metal on TMC and MTPC, respectively. As is evident from these results, TMC and MTPC have a higher selectivity for palladium(II), gold(III), and platinum(IV) than PMC reported earlier.[4] This is because PMC adsorbed copper(II), nickel(II), and cadmium(II) to some extent while it did not quite adsorb cobalt(II), zinc(II), manganese(II), and iron(III), however, TMC and MTPC have not quite adsorbed all of these metals described above.

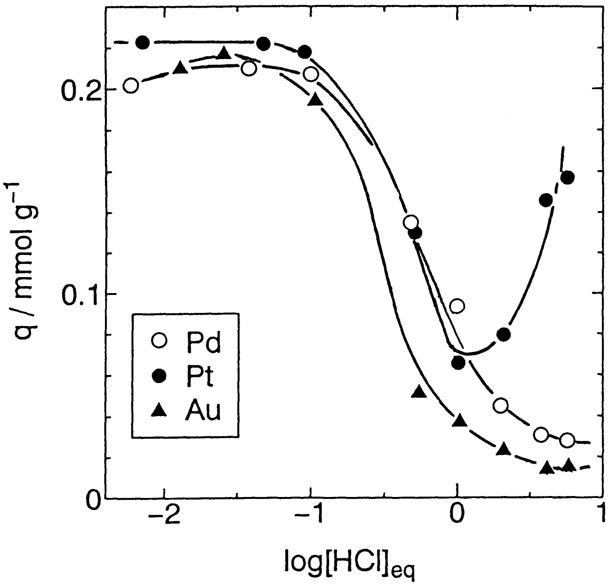


Fig.1. Effect of the hydrochloric acid concentration on the amount of metals adsorbed on TMC.

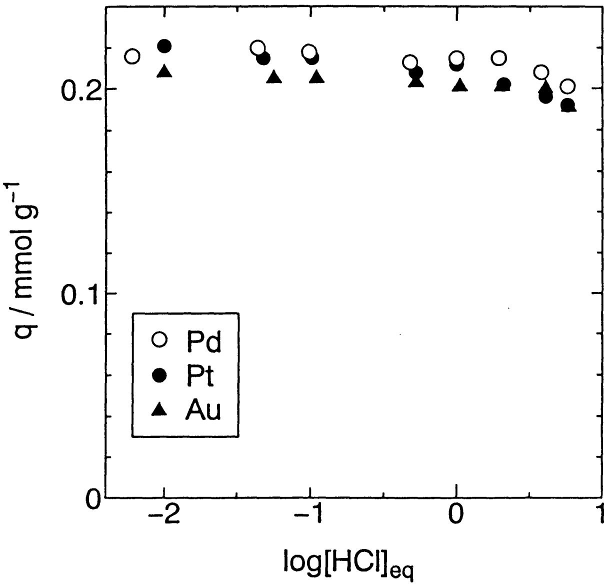


Fig.2. Effect of the hydrochloric acid concentration on the amount of metals adsorbed on MTPC.

Figure 3 shows the adsorption isotherms of palladium(II) from 0.01 mol dm^{-3} hydrochloric acid on TMC and MTPC, and that of the crosslinked chitosan obtained according to the method of Ohga et al.[7)] for comparison. The adsorption capacities for palladium were 4.8 mmol g^{-1}, 5.8 mmol g^{-1}, and 2.1 mmol g^{-1}, respectively; the adsorption capacity of sulfur-containing chitosan derivatives newly developed in the present study is about 2.5-3 times that of the crosslinked chitosan. The results mentioned above suggest that the present chitosan derivatives were crosslinked without a significant lowering of the adsorptive activity, and that the sulfur atom takes part in the adsorption of precious metals.

Consequently, the adsorption characteristics of TMC and MTPC, which were synthesized by crosslinking the corresponding intermediates protecting amino group by the Schiff base with (chloromethyl)oxirane, are expected to be applicable to the commercial separation and purification of palladium(II), gold(III), and platinum(IV) as the selective adsorbent from hydrochloric acid containing base metals.

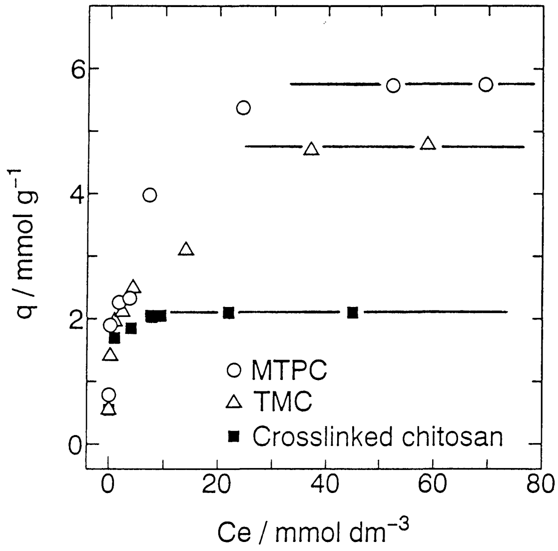


Fig.3. Adsorption isotherms of palladium(II) on MTPC, TMC, and crosslinked chitosan.

References

1) K. Tanaka, "Industrial Rare Metals," 74, 119 (1981).
2) R.A.A. Muzzarelli, F. Tanfani, M. Emanuelli, and S. Mariotti, Carbohydr. Res., 107, 199 (1982).
3) R.A.A. Muzzarelli and A. Zattoni, Int. J. Biol. Macromol., 8, 137 (1986).
4) Y. Baba and H. Hirakawa, Chem. Lett., 1992, 1905.
5) A. Hase, T. Kawabata, and K. Terada, Anal. Sci., 6, 747 (1990).
6) R.G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).
7) K. Ohga, Y. Kurauchi, and H. Yanase, Bull. Chem. Soc. Jpn., 60, 444 (1987).

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